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Substrate directed self-assembly of anisotropic nanoparticles

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HIGHLIGHTS

- Molecular dynamics study on the self-assembly of anisotropic nanoparticles on a flat surface.
- Anisotropic particles induce directionality in the assembly process.
- Aggregation of anisotropic particles depends on their shape and size.
- A flat surface can drive linear aggregation of adsorbed tetrahedrons.
- Phase diagrams of tetrahedrons and triangles on a surface are presented.

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ABSTRACT

We present a molecular dynamics study on the self-assembly of anisotropic nanoparticles—triangles and tetrahedrons on a flat surface. We observe ordered and disordered aggregates of nanoparticles depending on the particle–particle and surface–particle interactions. Anisotropic particles induce directionality in the assembly process. In particular, a cross over from the isotropic (spherical) assembly to the anisotropic (non-spherical) assembly of nanoparticles is identified as their size increases for weak nanoparticle–surface interactions. However, at strong nanoparticle–surface interactions, clusters of nanoparticles grow uniformly on the surface. We present phase diagrams that depict all possible structures of triangles and tetrahedrons depending on their size (L) and the nanoparticle–surface interaction strength (ε_{ns}). We show a disorder to order transition in the $L-\varepsilon_{ns}$ plane, as L and ε_{ns} increase.

1. Introduction

A remarkable variety of anisotropic colloidal nanoparticles (NPs)—cubes, rods, tetrahedrons, plates, tetrapods, octapods, bipyramids, janus particles, and many other shapes are synthesized in past few years (Glotzer and Solomon, 2007; Greyson et al., 2006; Ahmadi et al., 1996; Yamamuro et al., 2008). These particles have potential applications in photonics, energy storage devices, biological sensors, and many other micro/nanofluidic applications (Glotzer, 2004; Arciniegas et al., 2014; Stam et al., 2014). Vertically aligned nanopillers over a substrate, for example, is found to be a promising candidate for highly localized fluorescence imaging of single molecules (Xiea et al., 2011). Nanowires and nanotubes are used for building circuits in nanoscale electronics and optoelectronic devices (Duan et al., 2001). In addition, they find application in solar energy harvesting (Wanga et al., 2010), and are useful obstacles in nanodevices for separation of biomolecules (Seo et al., 2004). Similarly, optical, electrical, mechanical and catalytic properties of NPs of highly symmetric platonic shape, such as polyhedrons, could be tuned for specific applications (Kim et al., 2004; Millstone et al., 2009; Chan et al., 2008). Polyhedrons have preferred symmetry for 2D and 3D packing, which leads to many diverse structures and properties. Polyhedral shaped CdTe NPs, in a solution, self-assemble into a free floating sheet that displays considerable mechanical robustness (Tang et al., 2006). Further, polyhedral NPs show superior optical properties compared to spherical particles (Kasture et al., 2010). The optical properties of polyhedral gold nanoparticles also depend on their shape and size (Seo et al., 2008).

Therefore, the self-assembled structures of anisotropic particles have variety of interesting properties. In addition, certain viruses and other biological micro-organisms are of non-spherical geometry (Arkhipov et al., 2006). Hence, there is a growing research interest to study how the anisotropic particles interact among each other and with surfaces for understanding numerous biophysical processes and bio/nanotechnological applications (Li et al., 2011; Kinge et al., 2008;

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Min et al., 2008; Grzelczak et al., 2010). The challenge is to assemble NPs into required structures to obtained desired properties. The ability to assemble NPs into a desired structure depends on the understanding and controlling of the inter-particle interaction (Bishop et al., 2009). Computer simulations can play an important role in the understanding of the inter-particle interaction of nanoparticles, and eventually predicting the phase behavior of NPs. Indeed, molecular simulations have revealed that the anisotropic interaction in bulk systems can lead to highly structural materials (Patra and Singh, 2014; Zhang et al., 2003; Zhang and Glotzer, 2004). However, the effects of surfaces/substrates on the structures of anisotropic particles are not well studied. A few examples have appeared where the assembly of NPs on a surface is greatly influenced by the structural details of the surface and the shape of NPs. For example, rod-like arrangements of gold NPs on a silicon surface are predominantly aligned along the principle crystallographic axis of the surface (Hayton et al., 2007). The asymmetrical van der Waal interaction is found as a powerful means to control orientation of multi-component cylindrical arrays on a stationary substrate (Smith et al., 2014). More complex structures form on non-stationary substrate such as membranes. For example, the equilibrium arrangement of rod-like NPs on a membrane is affected by the orientation-dependent interaction between them and dynamical traps caused by incorrect arrangements (Yue et al., 2013). Also, the wrapping of a non-spherical micro-organism on a cellular membrane is largely dependent on its aspect ratio (Dasgupta et al., 2014). Therefore, it is evident that the structural properties of nanoparticles on a substrate strongly influenced by their shape. In spite of few works on the behavior of anisotropic particles, mainly nanorods, on a surface, their aggregation mechanism is not well studied.

The objective of this study is to understand the aggregations of non-spherical particles on a surface, which are revealed in recent experiments (Bishop et al., 2009; Wang et al., 2007; Radha and Kulkarni, 2011). Experiments have shown that nanoparticles aggregate into varieties of superstructures (Ghezelbash et al., 2004). For example, pyramidal SnO_2 nanoparticles epitaxially grow on a surface of single crystalline ZnO nanobelts with different orientations (Wang et al., 2007). In addition, triangular microplates of Au self-organize into well-formed single crystalline triangles on a Si surface, and sometime plates are held vertically on the surface during the growth event (Radha and Kulkarni, 2011). Superstructures are very sensitive to the shape of nanoparticles. In a recent experiment study, Ming et al. have shown that Au nanorods, polyhedra, nanocubes and bipyramids aggregates into nematic/smetic-A, hexagonally packed, tetragonally packed, and nematic/3D ordered super structures, respectively (Ming et al., 2008). However, the growth mechanism is not well understood. Both anisotropic and isotropic growths are observed for non-spherical nanoparticles (Ahmadi et al., 1996; Kasture et al., 2010; Loudet et al., 2005; Camargo et al., 2010; Rycenga et al., 2008; Mu et al., 2012). In this work, we have studied the quantitative details of the inter-particle and surface–particle interactions that lead to the aggregation of non-spherical particles into larger isotropic or anisotropic structures. The packing of particles also depends on their shape (Li et al., 2011; Graaf et al., 2011; Damasceno et al., 2012; Henzie et al., 2012). Hard tetrahedrons are found to pack into pentagonal dipyramid, icosahedrons, nonamers and tetrahelixes depending on the applied pressure (Haji-Akbari et al., 2009). Tetrahedrons are usually packed in ordered structures in presence of an external field. However they spontaneously exhibit disorder and loose packing (Baker and Kudrolli, 2010). Thus, the aim of the current work is to study the self-assembly process of NPs and their packing on a flat substrate using molecular dynamics (MD) simulations. We have considered two different shapes namely tetrahedron and triangle in this study.

A NP contains hundred to millions of atoms depending on its size and chemical composition. The self-assembly of NPs is a slow process; therefore, it is computationally very expensive to perform all-atom simulations of the self-assembly of NPs on a surface. In the present study, we use coarse-grained models, in which group of atoms within a NP are replaced by a single coarse-grained bead, thereby presenting a larger scale description of the system.

The rest of the paper is organized as follows. The models of tetrahedron and triangle are presented along with the model of the substrate in Section 2. Section 2 also describes the simulation details. Results are presented and discussed in Section 3. Finally, the conclusions are drawn in Section 4.

2. Model and methods

We use coarse-grained models to represent triangle and tetrahedron. We construct a lattice structure according to the shape of a NP. A triangular lattice and an fcc lattice are used for triangular and tetrahedral NPs, respectively. Each lattice site represents a coarse-grained bead of a NP. The distance between two neighboring beads is σ. One NP is made of several frozen beads as shown in Fig. 1. The number of beads in a NP of edge length $L = l\sigma$ is given by $l(l+1)/2$ for triangle and $l(l+1)(l+2)/6$ for tetrahedron, where l is a positive integer. Our aim is to study the generic behavior of anisotropic nanoparticles, rather than a specific system. We, therefore, model the interaction between coarse-grained beads by an empirical pair potential. Any two beads from different NPs interact via the Lennard–Jones (LJ) potential,

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - V(r_c). \quad (1)$$

Here, ε is the characteristic energy parameter. The pair potential represents dispersive and excluded volume interactions that are the characteristic of many NP systems (Patra and Singh, 2014; Zhang et al., 2003; Patra and Singh, 2013). We choose the cut-off distance $r_c = 2 \times 2^{1/6}\sigma$ to represent attractive interaction between NPs. The substrate is modeled as the (1 1 1) plane of an fcc lattice. Surface atoms are placed at lattice sites with neighbor distance of 1σ. The geometry of the flat surface is square. The system is periodic along the plane of the flat surface (xy-plane). Attractive surface–NP interactions are chosen to model adsorption of the NPs. NP beads and surface atoms interact through the LJ potential (cf. Eq. (1)) with the cut-off distance $r_c = 2 \times 2^{1/6}\sigma$. The interaction strength between the surface and NPs ε_{ns} is varied in this work. Surface atoms are also kept frozen in this work. The equations of motion are integrated with a time step of $0.01\tau_0$, where $\tau_0 = \sigma\sqrt{m/\varepsilon}$ is the unit of time and m is the mass of a bead of NPs. At each time step, frozen subunits of a NP move together as a rigid body using the method of quaternion (Miller et al., 2002). All the simulations are performed at a temperature $T = 1.0\varepsilon/k_B$, imposed using a Langevin thermostat (Zhang et al., 2003). Here, k_B is the Boltzmann constant. We have melted initial configurations at a

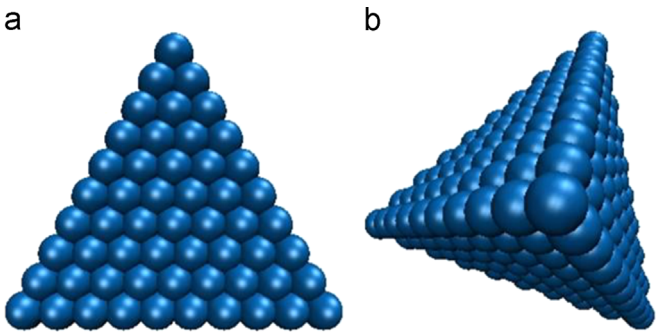

Fig. 1. Schematic representations of model NPs studied in this work: (a) triangle, and (b) tetrahedron.